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April 28, 2021

Ms. Karlene Fine
Executive Director
North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
Bismarck, ND 58505-0840

Dear Ms. Fine:

Subject: Quarterly Project Status Report Entitled "Low-Pressure Electrolytic Ammonia Production"; Contract No. R-036-45; EERC Fund 23228

Attached is a copy of the subject project status report for the period of January 1 through March 31, 2021.

If you have any questions, please contact me by phone at (701) 777-2982 or by e-mail at taulich@undeerc.org.

Sincerely,

DocuSigned by:
Ted Aulich
89B1B8E4D0E7430...

Ted R. Aulich
Principal Process Chemist
Fuels and Chemicals

TRA/kal

Attachment

c/att: Andrea Holl Pfennig, North Dakota Industrial Commission

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

Quarterly Project Status Report

(for the period of January 1, 2021, through March 31, 2021)

Prepared for:

Karlene Fine

North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
Bismarck, ND 58505-0840

Contract No. R-036-45

Prepared by:

Ted R. Aulich

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

April 2021

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ACKNOWLEDGMENT

This material is based upon work supported by the DOE National Energy Technology Laboratory under Award No. DE-EE0008324.

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EXECUTIVE SUMMARY

This quarterly report summarizes January–March 2021 progress made toward achieving milestones and objectives of the low-pressure electrolytic ammonia (LPEA) project under way at the University of North Dakota (UND) Energy & Environmental Research Center (EERC). Partners on the 3-year (June 2018 – July 2021) project include North Dakota State University (NDSU), Nel Hydrogen (formerly Proton OnSite), and the North Dakota Industrial Commission (NDIC). The project goal is to demonstrate an ammonia production energy reduction of at least 16% by replacing state-of-the-art (2018) high-pressure Haber–Bosch (HB)-based ammonia synthesis with the EERC-developed LPEA process. Achieving this energy reduction goal requires improving the proton conductivity, gas impermeability, and durability of the EERC–NDSU-developed polymer–inorganic composite (PIC) proton exchange electrolyte, a critical LPEA process component capable of high proton conductivity at 300°C. The foundation of the PIC electrolyte is an EERC-identified inorganic proton conductor referred to as "IPC2." Key accomplishments of the January–March 2021 quarter include the following:

- Devising and deploying a heat treatment/sintering technique to yield IPC2-based electrolyte disks that consistently deliver high (>0.01 S/cm) proton conductivity for over 40 hours at 300°C.

- Definitively demonstrating—via heated-stage x-ray diffraction (XRD) analysis—that IPC2 is thermochemically stable (no changes to crystallinity or composition) at temperatures of up to 600°C in the presence of humidity.

The EERC holds an unwavering commitment to the health and well-being of its employees, partners and clients, and the global community. As such, precautionary measures have been implemented in response to Covid-19. Staff continue to carry out project-related activities remotely, and personnel supporting essential on-site laboratory and testing activities are proceeding under firm safety guidelines. Travel has been minimized, and protective measures are being undertaken for those who are required to travel. At this time, work conducted by EERC employees is progressing with minimal schedule disruption. Challenges posed by economic variability will be met with open discussion between the EERC, the U.S. Department of Energy (DOE) Project Manager, and other partners to identify solutions. The EERC is monitoring developments across the nation and abroad to minimize risks, achieve project goals, and ensure the success of our partners and clients.

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION
Quarterly Project Status Report
January 1 – March 31, 2021

PROJECT GOALS/OBJECTIVES

The project goal is to demonstrate an ammonia production energy reduction of 16% by replacing state-of-the-art (2018) high-pressure HB-based ammonia synthesis with the EERC-developed LPEA process, as shown in Figure 1. To achieve the 16% production energy reduction target will require improving the LPEA process, which will require improving the PIC proton exchange membrane electrolyte on which the LPEA electrochemical cell is based. As a result,

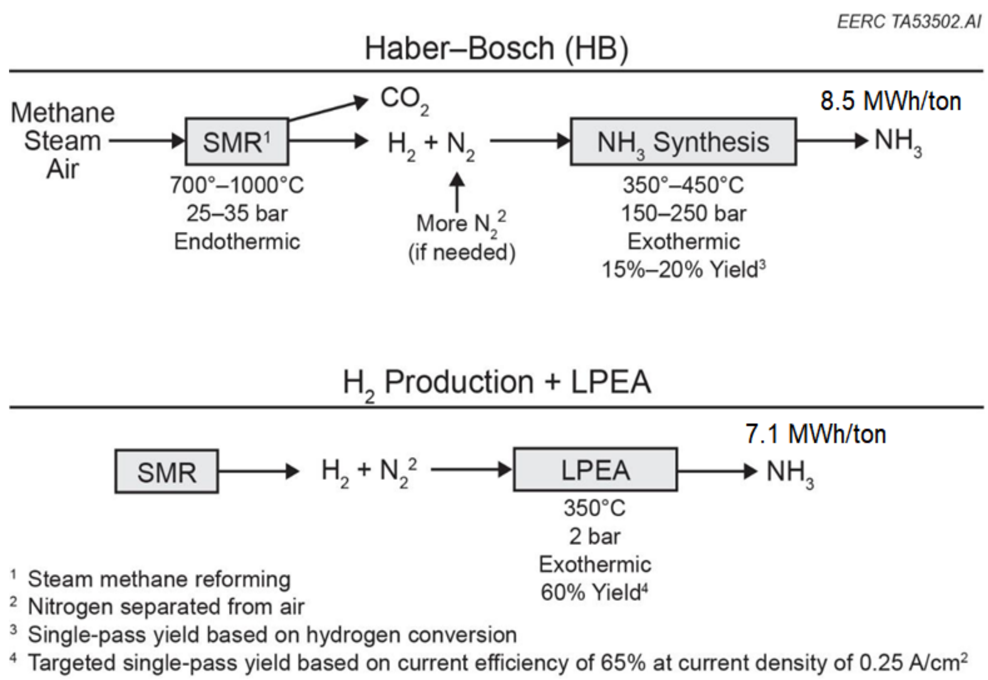

Figure 1. State-of-the-art (2018) HB versus LPEA-based NH_3 production.

the project is focused on improving the performance and durability of the PIC electrolyte, with the objective of producing a membrane/electrolyte that exhibits the following properties:

- Proton conductivity of $\geq 10^{-2}$ siemens/centimeter (S/cm) and gas permeability of <2% at a minimum temperature of 300°C.

- Ability to sustain 10^{-2} S/cm proton conductivity for at least 1000 hours (h).

- Mechanical strength (at 300°C) comparable to that of a commercial proton exchange-based electrolyzer membrane.

- As measured in a membrane–electrode assembly (MEA) at a minimum temperature of 300°C, current efficiency of ≥65% for NH_3 formation at a current density of ≥0.25 amps/cm^2 (A/cm^2), NH_3 production energy efficiency of ≥65%, and ≤0.3% performance degradation per 1000 h of operation.

BACKGROUND

In support of DOE Energy Efficiency and Renewable Energy (EERE) Advanced Manufacturing Office (AMO) goals to reduce life cycle energy consumption of manufactured goods and more cost-effectively use hydrogen in manufacturing processes, this project is focused on optimizing and demonstrating the improved efficiency (versus HB ammonia production) of the EERC-developed LPEA production process. Because it does not require the high pressure and high recycle rate (because of low single-pass ammonia yield) of the HB process, LPEA offers the potential for significant reduction in both energy consumption and cost. Partners on the proposed project are NDSU, Nel Hydrogen (Nel) (formerly Proton OnSite), the UND Chemistry Department, and NDIC. The LPEA process is based on an innovative EERC-developed PIC high-temperature proton exchange electrolyte. The process operates at ambient pressure and a temperature of 300°C and uses inputs of hydrogen, nitrogen, and electricity to make ammonia. The EERC demonstrated LPEA process viability in ammonia formation tests conducted using a 0.2-watt electrochemical cell built around an early-stage PIC membrane electrolyte.

To meet the above-listed electrolyte performance and durability specifications, the project initially targeted fabrication—via a "coelectrospinning" technique—of a PIC membrane comprising "core–shell" inorganic proton conductor–polybenzimidazole (IPC–PBI) proton-conducting nanofibers contained within and aligned perpendicularly to the plane of a PBI matrix/membrane, as shown in Figure 2. Because each fiber core would comprise a chain of IPC particles in contiguous contact with one another throughout the chain length, each fiber would essentially function as a high-efficiency proton transport conduit running straight through the membrane. However, during Budget Period 1 (BP1) of the project, an alternative IPC was identified that offered significantly improved proton conductivity, stability, and durability—at 300°C—than the originally proposed IPC. Because this new IPC (IPC2) encompasses chemical and physical properties not amenable to coelectrospinning with PBI to yield core–shell nanofibers, new methods for IPC2 deployment as an electrolyte are being pursued. Current focus is on the use of heat treatment/sintering techniques to yield durable IPC2-based thin-disk electrolytes.

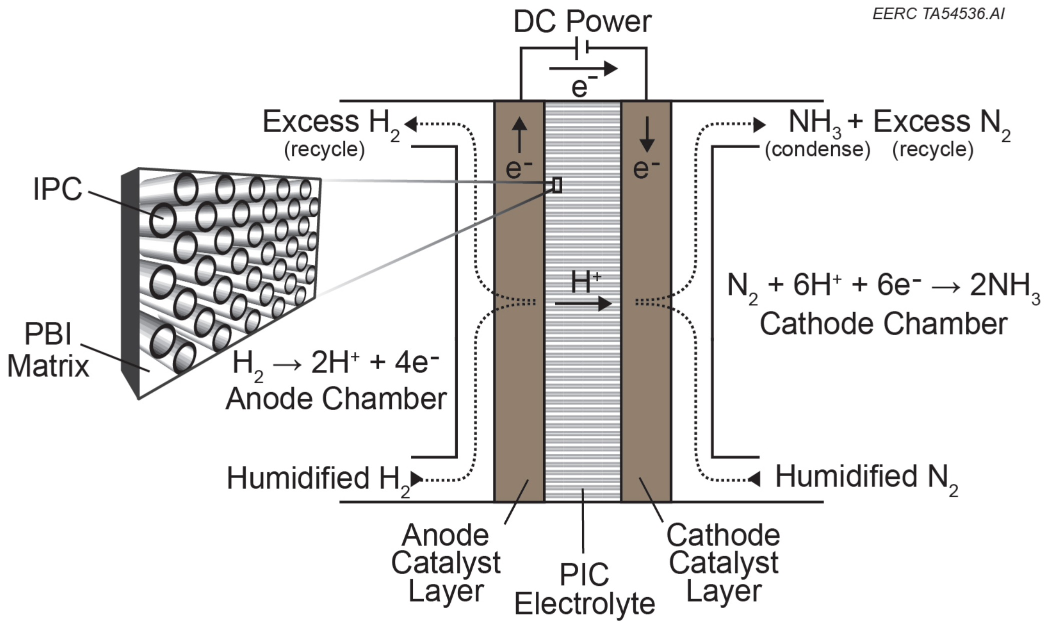

Figure 2. LPEA process.

Following fabrication of an IPC2-based electrolyte that meets performance and durability specifications, the electrolyte—along with selected anode and cathode catalysts—will be used to construct experimental MEAs. MEAs will be incorporated into LPEA unit cells that will be evaluated based on NH_3 formation efficiency and durability, with the objective of identifying an optimal MEA configuration. The optimal MEA configuration will be used as the basis for building a stack of several LPEA unit cells that will compose an LPEA system capable of producing at least 100 grams/day (g/d) of NH_3. The 100-g/d LPEA system will undergo optimization and then be used to demonstrate NH_3 synthesis (from H_2) at the LPEA target production energy input requirement of 0.8 megawatt hours (MWh/ton), which would translate to a total (H_2 production plus NH_3 synthesis) LPEA-based NH_3 production energy input requirement of 7.1 MWh/ton, the project goal. LPEA system operation and performance data will be used to perform a techno-economic evaluation of the LPEA-based NH_3 production process.

ACCOMPLISHMENTS

Key accomplishments during the January–March 2021 reporting period include the following:

- Devising and deploying a heat treatment/sintering technique to yield IPC2-based electrolyte disks that consistently deliver high (>0.01 S/cm) proton conductivity for over 40 hours at 300°C.

- Definitively demonstrating—via heated-stage XRD analysis—that IPC2 is thermochemically stable (no changes to crystallinity or composition) at temperatures of up to 600°C in the presence of humidity.

PROGRESS AND STATUS

Task 1 – Project Management

In response to a request from the EERC, a 6-month no-cost project extension was officially approved by the Project Contract Officer. The project end date is now 31 December 2021. Based on findings indicating that IPC2 particle-size reduction via planetary ball milling in an appropriate fluid translated to significant improvement in 1) IPC2 proton conductivity and 2) IPC2 particle "sinterability" (enabling fabrication of more dense, durable, and gas impermeable electrolytes), procurement of a planetary ball mill was initiated. Project funds will not be used for the procurement. Table 1 summarizes the status of each project task.

Table 1. Task Schedule – BP2

Task No.	Task Description	Task Completion Date			Task Progress Notes
		Original Planned	Revised Planned	% Complete	
1	Project Management	June 2021	Dec. 2021	83	Project extension approved, end date now 31 Dec. 2021.
3	Optimize IPC and PIC membrane performance and durability	Dec. 2020	Sept. 2021	85	Performance target met, still working on durability.
5	Screen cathode catalysts, fabricate MEAs, deploy MEAs in unit cell for LPEA process optimization	Dec. 2020	Sept. 2021	85	Catalysts screened; MEA and unit cell work ongoing.
6	Design, fabricate, and optimize 100-g/d LPEA system; acquire data for techno-economic analysis	March 2021	Sept. 2021	10	Task work initiated in January 2021.
7	Conduct techno-economic analysis	June 2021	Dec. 2021	0	Not started.

Task 3 – Optimize IPC and PIC Membrane Performance and Durability

A thin-disk electrolyte fabricated by pressurized sintering of IPC2 particles was evaluated with the objective of demonstrating fulfillment of Milestone 3.4 performance requirements. While meeting milestone proton conductivity and thermal decomposition targets ($\geq 10^{-2}$ S/cm and <3%, respectively, at 300°C in optimal humidity), the gas permeability target of <2% hydrogen crossover was unmet because of measurement system failure during establishment of baseline permeability at room temperature. Hydrogen crossover/permeability was measured by supplying a constant flow of pure hydrogen and nitrogen to a unit cell anode and cathode chamber, respectively, separated by an electrolyte, and monitoring hydrogen concentration in the cathode chamber using a calibrated laser gas analyzer. Figure 3 shows <2% hydrogen permeation through the electrolyte (from anode to cathode) for roughly 90 minutes, at which point hydrogen began flowing around the electrolyte via a system leak. An improved method for measuring hydrogen crossover is being developed.

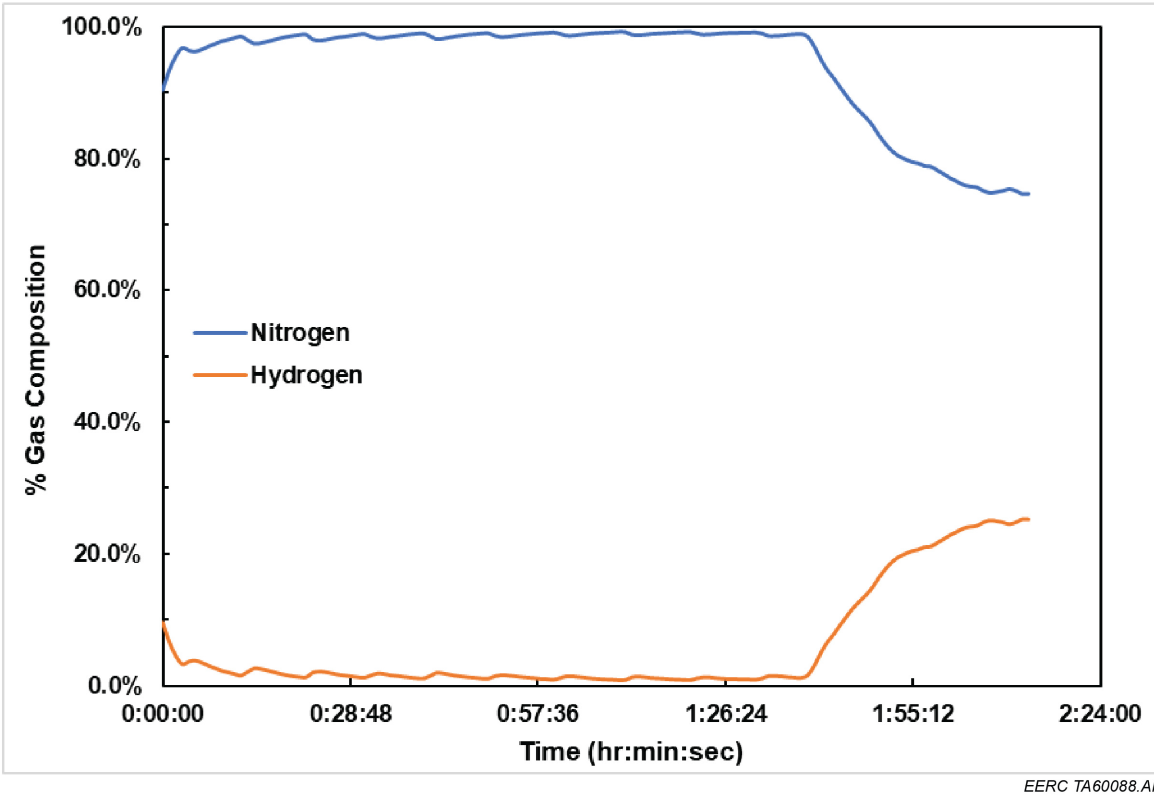

Figure 3. Hydrogen crossover from anode to cathode (at room temperature), as measured by hydrogen cathode concentration.

Although IPC2 has been shown to offer excellent proton conductivity (from 0.01 to 0.06 siemens per centimeter [S/cm]) at 300°C in the presence of steam, maintaining proton conductivity over time has proven to be difficult. To ensure that conductivity decline is not due to IPC2 decomposition or degradation, a series of heated-stage XRD tests were conducted. IPC2 particles were mounted on the XRD stage, temperature was ramped up to 600°C in 30°C intervals, and XRD patterns were acquired at each 30° increment. Temperature was then ramped down in 30° intervals and data acquired accordingly. Throughout the complete up–down cycle, IPC2 particles were exposed to humidified nitrogen in the form of nitrogen bubbled through a 50°C water bath. Figures 4 and 5 indicate that exposure to high-temperature steam has no impact on IPC2 crystallinity or composition. Because IPC2 is stable in steam at 300°C, the observed gradual decline in IPC2-based electrolytes is likely due to improper deployment of IPC2 particles in the electrolyte configurations evaluated to date. As examples, breakdown and/or decomposition of PBI (in PBI-matrix-based electrolytes) and inadequate bonding in sintered IPC2 electrolytes could result in gradual development of gas channels that negatively impact proton conductivity.

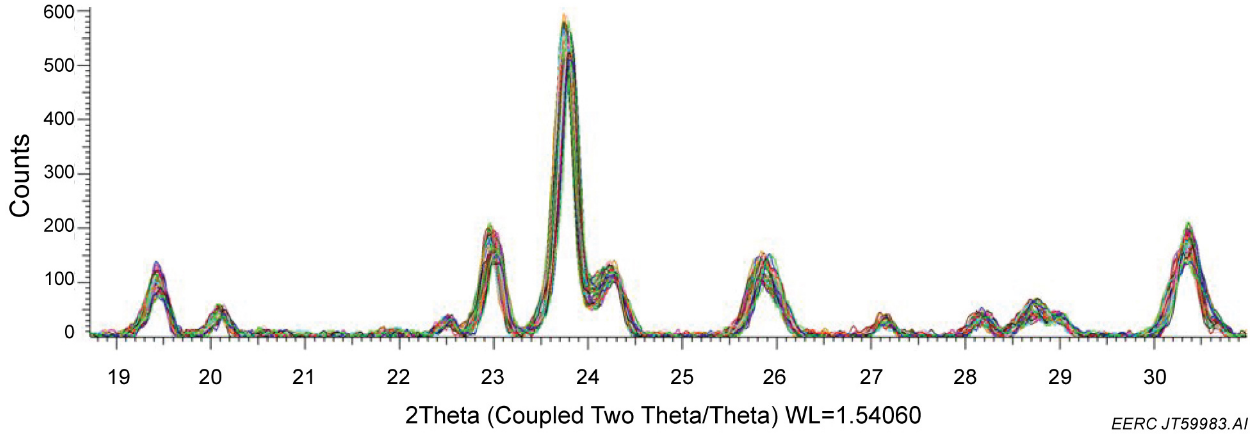

Figure 4. Overlain diffraction patterns for IPC2 from 30° to 600°C to 30°C (in 30° increments) under humidified nitrogen. Lateral shift due to thermal expansion of IPC2 crystals.

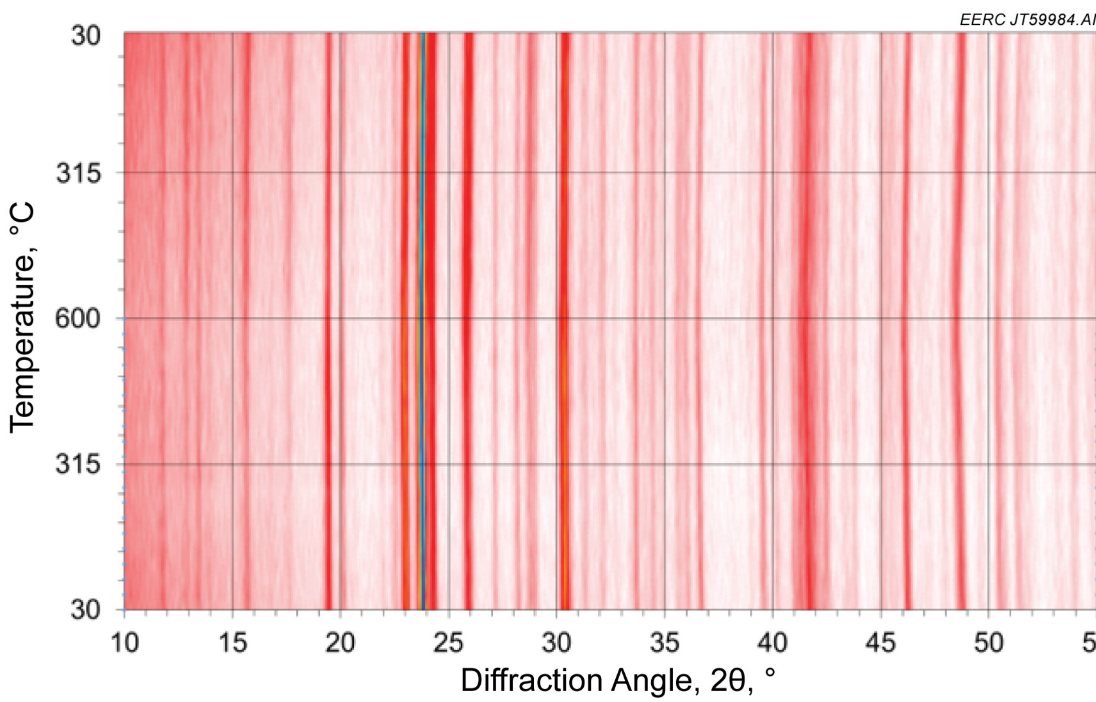

Figure 5. XRD history of IPC2 from 30°C to 600°C to 30°C. Color indicates diffraction signal height. No new phases form; IPC2 structure appears stable, exhibiting only thermal expansion.

Task 5 – Catalyst Screening and MEA/Unit Cell Development and Optimization

A set of Nel-fabricated MEAs comprising membrane (75% IPC2–25% PBI), niobium nitride cathode, and platinum anode were evaluated and found to provide inadequate proton conductivity. As a result, a decision was made to fabricate MEAs using PBI matrix-based thin disks (rather than membranes) as electrolyte. Although not as immediately compatible with Nel membrane-based MEA fabrication techniques, thin-disk electrolytes have been shown to consistently provide higher and more sustainable proton conductivity than PBI matrix-based membranes. After tailoring the MEA fabrication method as needed, disk-electrolyte-based MEAs were fabricated by Nel and are awaiting evaluation by the EERC.

Task 6 – Design, Fabrication, and Operation of 100-g/d LPEA System

Design work was initiated based on the use of thin disks rather than membranes as electrolyte.

Task 7 – Techno-Economic Analysis

No activity this quarter.

PLANS FOR NEXT QUARTER

Task 3 – Optimize IPC and PIC Membrane Performance and Durability

Optimization of methods for fabrication, evaluation, and optimization of PIC thin-disk electrolytes will continue, with emphasis on using heat treatment/sintering techniques to yield durable disks comprising at least 95 weight% IPC2.

Task 5 – Catalyst Screening and MEA/Unit Cell Development and Optimization

Additional MEAs will be fabricated and evaluated based on ammonia synthesis rate and current efficiency.

Task 6 – Design, Fabrication, and Operation of 100-g/d LPEA System

Advance design of 100-g/d system.

Task 7 – Techno-Economic Analysis

Develop strategy/deployment scenario for economically competitive initial entry of LPEA into the commercial ammonia industry.

PRODUCTS

None.

IMPACTS

Impact on Technology Transfer and Commercialization Status

No commercialization impacts, progress, issues, or concerns to report during this quarter.

Dollar Amount of Award Budget Being Spent in Foreign Country(ies)

No spending of any project funds in any foreign countries has occurred or is planned.

CHANGES/PROBLEMS

The EERC is operational and open for business. Personnel that are not essential for on-site operations have transitioned to working from home. Essential project, laboratory, and field-based activities are proceeding with the incorporation of the Centers for Disease Control and Prevention, the state of North Dakota, and UND guidelines associated with COVID-19, and mitigation measures have been implemented. In collaboration with project partners, the EERC is continually assessing potential impacts to project activities resulting from COVID-19 and/or the U.S. economic situation. As of the date of this report, the EERC is planning to phase in on-site work starting in July 2021.

Scope Issues, Risks, and Mitigation Strategies

None.

Actual or Anticipated Problems or Delays and Corrective Actions or Plans to Resolve

To accommodate the approximate 6-month progress delay, a 6-month no-cost extension was requested. The request was approved, and the project end date is now 31 December 2021.

Changes That Have a Significant Impact on Expenditures

None.

RECIPIENT AND PRINCIPAL INVESTIGATOR DISCLOSURES

None.

CONFLICTS OF INTEREST WITHIN PROJECT TEAM

None.

PARTNERS AND FINANCIAL INFORMATION

This project is sponsored by NDIC, DOE, UND Chemistry, NDSU, and Proton. Table 2 shows the total budget of $3,164,010 for this project and expenses through the reporting period.

Table 2. Project-to-Date Financial Report at March 31, 2021

Funding Source	Budget	Current Reporting Period Expenses	Cumulative Expenses as of 12/31/20	Remaining Balance
DOE	$2,497,983	$136,604	$1,973,010	$524,973
UND Chemistry – In Kind	$69,027	$0	$69,027	$0
NDIC	$437,000	$46,592	$381,086	$55,914
NDSU – In Kind	$120,000	$0	$120,000	$0
Proton – In Kind	$40,000	$1,645	$18,591	$21,409
Total	**$3,164,010**	**$184,841**	**$2,561,714**	**$602,296**